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## ABSTRACT

In situ FTIR spectroscopy is employed to study the adsorption of cyanide ion ( $\text{CN}_{\text{ads}}^-$ ) within the double-layer region on a polycrystalline palladium surface in aqueous perchlorate ( $0.10\text{M NaClO}_4$ ) electrolyte. Four surface infrared bands in the  $1800$  to  $2200\text{cm}^{-1}$  range are observed. Surface bands with peak maxima seen at about  $2060$  and  $1980\text{cm}^{-1}$  are assigned to linear and bridge-bound  $\text{CN}_{\text{ads}}^-$ , respectively. Two additional bands near  $2150$  and  $2200\text{cm}^{-1}$  are attributed to Pd/CN surface films. The relative intensities of the bands due to linear and bridged  $\text{CN}_{\text{ads}}^-$  suggest the predominance of the bridge-bound adsorbate on palladium. The experimentally observed frequency potential dependence ( $d\nu_{\text{C-N}}/dE$ ) for the bridged cyanide adsorbate ( $20\text{cm}^{-1}\text{V}^{-1}$ ) is greater than that for the linearly adsorbed species ( $12\text{cm}^{-1}\text{V}^{-1}$ ). Potential dependencies of the infrared frequencies due to linear and bridged  $\text{CN}_{\text{ads}}^-$  show little variation with changes in cyanide concentration. Possible explanations for the predominance of bridged bonding are given, along with a discussion of the formation and depletion of surface Pd/CN films. A classical theoretical model, employed previously in the analysis of adsorbed carbon monoxide on platinum, is used to estimate frequencies and potential dependencies of the C-N stretch for linear and bridged  $\text{CN}_{\text{ads}}^-$  on a palladium surface.

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**Technical Report No. 26**

**AN INFRARED SPECTROELECTROCHEMICAL STUDY OF CYANIDE ADSORPTION  
ON PALLADIUM SURFACES**

**by**

**Kevin Ashley, Frederick Weinert, Mahesh G. Samant, H. Seki,  
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AN INFRARED SPECTROELECTROCHEMICAL STUDY OF CYANIDE  
ADSORPTION ON PALLADIUM SURFACES

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**ABSTRACT**

In situ FTIR spectroscopy is employed to study the adsorption of cyanide ion ( $\text{CN}_{\text{ads}}^-$ ) within the double-layer region on a polycrystalline palladium surface in aqueous perchlorate ( $0.10\text{M NaClO}_4$ ) electrolyte. Four surface infrared bands in the  $1800$  to  $2200\text{cm}^{-1}$  range are observed. Surface bands with peak maxima seen at about  $2060$  and  $1980\text{cm}^{-1}$  are assigned to linear and bridge-bound  $\text{CN}_{\text{ads}}^-$ , respectively. Two additional bands near  $2150$  and  $2200\text{cm}^{-1}$  are attributed to Pd/CN surface films. The relative intensities of the bands due to linear and bridged  $\text{CN}_{\text{ads}}^-$  suggest the predominance of the bridge-bound adsorbate on palladium. The experimentally observed frequency potential dependence ( $d\nu_{\text{C-N}}/dE$ ) for the bridged cyanide adsorbate ( $20\text{cm}^{-1}\text{V}^{-1}$ ) is greater than that for the linearly adsorbed species ( $12\text{cm}^{-1}\text{V}^{-1}$ ). Potential dependencies of the infrared frequencies due to linear and bridged  $\text{CN}_{\text{ads}}^-$  show little variation with changes in cyanide concentration. Possible explanations for the predominance of bridged bonding are given, along with a discussion of the formation and depletion of surface Pd/CN films. A classical theoretical model, employed previously in the analysis of adsorbed carbon monoxide on platinum, is used to estimate frequencies and potential dependencies of the C-N stretch for linear and bridged  $\text{CN}_{\text{ads}}^-$  on a palladium surface.

## INTRODUCTION

In recent years infrared spectroelectrochemistry has been shown to be invaluable for investigations involving the interaction of adsorbates with surfaces of electrodes.<sup>1</sup> A wide variety of physical and chemical phenomena can be studied in great detail by the use of in situ infrared (IR) spectroscopic surface probes of electrodes in electrochemical cells. Examples of such phenomena include electrocatalytic oxidation of organic acids,<sup>2</sup> potential-dependent adsorption and desorption of molecules and ions,<sup>2</sup> the electrochemically induced polymerization of conducting polymers,<sup>3</sup> and studies of dynamics in the electrode-electrolyte interfacial region.<sup>2,4</sup> A vast literature exists concerning the infrared spectroscopy of adsorbed carbon monoxide (CO) on solid electrodes,<sup>2</sup> and studies of this species have led to a very good understanding of adsorbate-electrode surface bonding, reactions and dynamics. There have also been a number of in situ IR spectroelectrochemical studies on adsorbed pseudohalide species such as cyanide (CN<sup>-</sup>),<sup>2,5</sup> azide (N<sub>3</sub><sup>-</sup>),<sup>2</sup> and thiocyanate (SCN<sup>-</sup>),<sup>2,4,6</sup> with goals toward understanding interfacial dynamical properties as well as comparisons with molecular adsorbate systems such as specifically adsorbed CO. Through the utilization of surface-sensitive in situ IR spectroscopy in electrochemical systems, it has become possible to obtain information concerning identification of species (i.e., reactants, intermediates, or products of electrode reactions) at or near smooth electrode surfaces. These observations were previously impossible by conventional electrochemical or other available spectroelectrochemical techniques (e.g., surface-enhanced Raman scattering<sup>7</sup>).

A significant advantage of spectroelectrochemical studies involving adsorbed pseudohalide species (such as CN<sup>-</sup> or SCN<sup>-</sup>) over similar studies involving adsorbed carbon monoxide is the wide double layer region available in certain pseudohalide systems. The double layer region is the potential region in which no faradaic reactions occur, and the electrode surface is said to be "ideally polarized".<sup>8</sup> For studies of interfacial

dynamics it is beneficial to conduct spectroelectrochemical experiments in the absence of redox reactions which can complicate spectral interpretations. In aqueous solutions containing CO the available double layer region is relatively narrow, for adsorbed carbon monoxide ( $\text{CO}_{\text{ads}}$ ) is more easily oxidized and reduced than, say, its isoelectronic pseudohalide counterpart, adsorbed cyanide ( $\text{CN}_{\text{ads}}^-$ ). Therefore studies of interfacial dynamical properties (which can be addressed by following the potential dependence of IR absorption frequencies of adsorbate vibrational bands<sup>1</sup>) are limited in scope if CO is the adsorbate species, since the available applicable potential range is limited. If the double layer region is not adhered to, spectra may be difficult to interpret due to the presence of other species and/or surface films produced by a surface-mediated electrochemical reaction. Hence for investigations of the potential dependencies of adsorbate IR bands it is of interest to examine pseudohalide systems such as  $\text{CN}_{\text{ads}}^-$  due to the wide double layer potential regions offered in these systems.

In a preliminary report<sup>5</sup> we noted striking differences in the potential-dependent IR spectroscopy (PDIRS<sup>9</sup>) of  $\text{CN}_{\text{ads}}^-$  on platinum vs. palladium surfaces within double layer potentials of both metals. Differences of this kind have been observed previously for the analogous case of  $\text{CO}_{\text{ads}}$  on Pt and Pd,<sup>10,11</sup> and have been attributed to differences in adsorbate-surface bonding interactions. In this work we report the results of a detailed study concerned with the adsorption of cyanide on smooth palladium electrodes, using surface infrared spectroscopy as an in situ probe of the interface. The surface infrared spectral frequencies for cyanide species adsorbed on palladium, as well as the potential dependencies of those frequencies, are then compared with theoretically evaluated frequencies using the model of Korzeniewski et al.<sup>12</sup>

## EXPERIMENTAL

The in situ IR spectroelectrochemical data were obtained by combining the polarization modulation technique (Fourier

transform infrared reflection absorption spectroscopy, or FT-IRRAS<sup>13</sup>) with a potential difference method (subtractively normalized interfacial Fourier transform infrared spectroscopy, or SNIFTIRS<sup>14</sup>). FT-IRRAS spectra were taken at the reference and sample potentials, and a difference spectrum was then obtained by ratioing the two absolute spectra obtained by polarization modulation. This served to optimize the surface specificity of the IR spectroscopic probe. The spectrometer employed was an IBM IR/98 instrument, with a globar IR source and liquid nitrogen-cooled indium antimonide detector (Infrared Associates). The IR spectroelectrochemical cell was a Kel-F external reflection cell, as described previously<sup>15</sup>, with a bevelled calcium fluoride window (Frank Cooke, Inc.). The bulk polycrystalline palladium mirror working electrode (Johnson-Matthey, 99.99% Pd) was polished mechanically with successively smaller grades (1.0, 0.3, and 0.05 microns, respectively) of polishing alumina (Buehler). This electrode was then polished electrochemically by repeated potential cycling. Surface-sensitive IR difference spectra were obtained by recording reference spectra (within the double layer potential region) at one potential and sample spectra at another potential; the incidence angle at the electrode surface was approximately 65° with respect to the surface normal. Typically 1000 spectra (approx. 1 second per scan) were recorded at each potential, with the voltage being switched every 32 scans to avoid surface contamination.

Electrode potential was controlled with a Princeton Applied Research 173/175/179 potentiostat system, and voltages were recorded against an Ag/AgCl (3 M KCl) reference (Microelectrodes, Inc.). NaCN and NaClO<sub>4</sub> (reagent grade) were obtained from Aldrich and promptly used as received. Deionized (Nanopure, 18 megohms), organic-free (Organopure) water was used to prepare all solutions, and electrolytes were degassed with pure nitrogen or argon before each experiment. Voltammetric data were recorded on an IBM model 7424 MT x-y plotter.



## RESULTS AND DISCUSSION

### Electrochemistry

Figure 1 shows representative cyclic voltammograms, obtained at a palladium electrode, for sodium perchlorate electrolytes (0.10 M  $\text{NaClO}_4$ ) with cyanide both present (Figure 1[a,b]) and absent (Figure 1[c]) from solution. If cyanide is present in the system, the voltammogram is essentially featureless, even for cyanide concentrations as low as 1mM (Figure 1[a]). This indicates that the electrode is "ideally polarized" over a wide potential range, i.e., a wide "double layer" region is said to exist if cyanide is present. It should be noted that very similar cyclic voltammograms were obtained between about -0.9V and +0.4V regardless of the cyanide concentration (for solutions containing 1, 5, and 25mM  $\text{NaCN}$ ). This suggests very strongly that cyanide is specifically adsorbed on the palladium surface over this potential range, even if the cyanide concentration in solution is quite low (e.g., less than 1mM). Capacitance data obtained on silver surfaces for  $\text{CN}^-$  in 1M  $\text{Na}_2\text{SO}_4$  indicate that cyanide is strongly adsorbed even at extremely negative potentials;<sup>16,17</sup> our voltammetric data on Pd in perchlorate electrolyte suggest cyanide adsorption to rather negative electrode potentials as well. Evidence for Pd/CN film formation is apparent in the increased anodic current observed at potentials more positive than +0.5V.  $\text{CN}^-$  depletion is also possible at these rather positive potentials, although this can only be confirmed by IR spectroelectrochemistry.

If cyanide is not present in the system (Figure 1[c]) the effective double layer voltage range is diminished considerably. Here an oxide layer is formed at relatively low positive potentials, and hydrogen adsorption and subsequent evolution occur at rather low negative potentials on this metal. These data show that cyanide is an effective poison of the palladium surface, preventing electroreduction and electrooxidation of solvent species (water) by the metal. These results are similar to voltammetric results obtained previously for thiocyanate adsorbed on a platinum electrode.<sup>4</sup> It is within this wide double

layer region between  $-1.0\text{V}$  and  $+0.5\text{V}$  or so that we desire to study the potential dependent behavior of the infrared bands due to surface cyanide species. As previously mentioned, this will enable in situ surface IR spectra to be interpreted more easily since complications from electrode mediated electron transfer processes are minimized.

### Infrared Spectroelectrochemistry

Figure 2 shows typical in situ IR difference spectra obtained in a  $5\text{mM}$  sodium cyanide /  $0.10\text{M}$  sodium perchlorate system (on palladium) as a function of the light polarization.<sup>5</sup> The reference and sample potentials were the same for solutions in which cyanide was either present or absent: the reference potential was  $-0.90\text{V}$  and the sample potential was  $+0.70\text{V}$  (vs.  $\text{Ag}/\text{AgCl}$ ). The potential-dependent infrared (PDIR) spectrum obtained with s-polarized radiation (Figure 2, dashed line) shows positive bands at  $2170$  and  $2135\text{ cm}^{-1}$ , as well as a series of bands due to rotational modes of background water vapor between  $1900$  and  $2000\text{ cm}^{-1}$ . The surface PDIR spectrum for  $5\text{mM}$   $\text{NaCN}$  in aqueous perchlorate electrolyte, obtained via polarization modulation (in order to maximize surface sensitivity), yields a series of bands in the  $1900$  to  $2300\text{ cm}^{-1}$  frequency range. Positive bands are observed at  $2135$ ,  $2065$ , and  $1980\text{ cm}^{-1}$ , and two negative bands appear at  $2202$  and  $2154\text{ cm}^{-1}$ . The results from s-polarized radiation indicate that the bands at  $2170$  and  $2135\text{ cm}^{-1}$  are due to species dissolved in solution; these bands are assigned to  $\text{Pd}(\text{CN})_6^{2-}$  and  $\text{Pd}(\text{CN})_4^{2-}$ , respectively.<sup>18</sup> Thus a solution band at  $2135\text{ cm}^{-1}$  still appears in the surface-sensitive PDIR spectrum, despite pains taken to omit solution features. The remaining bands are assigned to surface species. The surface bands at  $2202$  and  $2154\text{ cm}^{-1}$  are attributed to surface films of  $\text{Pd}/\text{CN}$ . These films appear to be precursors to the dissolved  $\text{Pd}/\text{CN}$  complexes that give rise to the two solution bands seen in the s-polarized spectrum. The band near  $2200\text{ cm}^{-1}$  is tentatively assigned to a surface film of  $\text{PdCN}$  or  $\text{Pd}(\text{CN})_2$ , while the surface feature near  $2150\text{ cm}^{-1}$  is attributed to a

precursor of the  $\text{Pd}(\text{CN})_4^{2-}$  solution complex, surface  $\text{Pd}(\text{CN})_4^{19}$ . The bands appearing at 2065 and 1980  $\text{cm}^{-1}$  are attributed to linear and bridge-bound  $\text{CN}^{\text{ads}}$ , respectively<sup>5</sup>; these types of adsorbates are schematized in Figure 3. The bonding of cyanide on a palladium surface is thus similar to the case of carbon monoxide adsorption on this metal;<sup>10,11</sup> both linear and bridged species for CO and  $\text{CN}^-$  (which are isoelectronic) are detected by surface infrared spectroelectrochemistry, and the band intensity of the bridged moiety greatly exceeds that of the linear bound species.

It is also of interest to note that the infrared band frequency of linearly adsorbed cyanide ( $\text{CN}^{\text{ads}}$ ) is less than that of the solution species. The IR frequency of cyanide ion dissolved in aqueous solution appears at about 2080  $\text{cm}^{-1}$ <sup>20</sup>, so an apparent decrease in bond order of the  $\text{C}\equiv\text{N}$  bond is observed for linear  $\text{CN}^{\text{ads}}$ . This contrasts with the case of cyanide adsorption on other noble metals such as platinum,<sup>5</sup> gold,<sup>21,22</sup> or silver,<sup>22,23</sup> in which the IR band frequency due to the normal C-N stretching mode ( $\nu_{\text{C-N}}$ ) from linear  $\text{CN}^{\text{ads}}$  is greater than that of solution cyanide. In a single electron molecular orbital picture this observation can be explained<sup>24</sup> by taking into account the differences in ionization potentials of the metals involved. For example, let us consider the case of cyanide adsorption on platinum vs. palladium. In Pd the work function and 4d band lie approximately 1eV above the work function and 5d band of Pt.<sup>24</sup> Thus Pt 5d back-donation to the  $\pi^*$  orbital of  $\text{CN}^{\text{ads}}$  is not as important as the 5 $\sigma$  donation from  $\text{CN}^{\text{ads}}$  to Pt. Hence,  $\nu_{\text{C-N}}$  is greater for adsorbed cyanide than for free  $\text{CN}^-$  in solution since the 5 $\sigma$  level is slightly antibonding. For Pd, the  $\sigma$  interaction is not as important as the  $\pi$  interaction; i.e., d $\rightarrow$ p  $\pi$  backbonding is favored over  $\sigma$  donation. Therefore  $\nu_{\text{C-N}}$  for linear  $\text{CN}^{\text{ads}}$  is less than that of free solution  $\text{CN}^-$ ; also, formation of the bridged  $\text{CN}^{\text{ads}}$  species is favorable, in keeping with our experimental observations. Similar arguments have been employed to rationalize the predominance of bridge-bonding of  $\text{CO}_{\text{ads}}$  on highly ordered rhodium surfaces.<sup>25</sup>

Another possible explanation for the decrease in band frequency of linear  $\text{CN}_{\text{ads}}^-$  (with respect to free solution  $\text{CN}^-$ ) can be offered by considering the degree of covalency of the metal-cyanide bond. If the adsorbate-metal bond is largely ionic, we would expect the band frequency of the adsorbed species to be shifted to higher energies when compared to the solution species;<sup>26</sup> this seems to be the case for linear  $\text{CN}_{\text{ads}}^-$  on a platinum surface.<sup>5</sup> Further evidence for ionic bonding of cyanide on platinum is suggested by possibility for binding through either carbon or nitrogen end down, as suggested by sum-frequency generation experiments<sup>27</sup> and FTIR spectroelectrochemistry.<sup>28</sup> A lack of evidence for N-bound species, as well as a decrease in band frequency for linear  $\text{CN}_{\text{ads}}^-$  on Pd (when compared to that for solution species), may be due to a metal-adsorbate bonding interaction that is more covalent than for linear  $\text{CN}_{\text{ads}}^-$  on Pt.

Surface in situ FTIR spectra are shown in Figures 4-6 for systems in which the cyanide concentrations are varied from 1 to 25mM. There are few apparent differences in the potential-dependent behaviors of the linear and bridged  $\text{CN}_{\text{ads}}^-$  species for differences in cyanide concentration (Figure 7). It is of interest to note that the frequency change with potential for the bridged surface cyanide exceeds that of the linearly adsorbed species. We find that  $d\nu_{\text{C-N}}/dE$  for linear  $\text{CN}_{\text{ads}}^-$  is approximately  $12 \text{ cm}^{-1}\text{V}^{-1}$ , while this quantity is on the order of  $20 \text{ cm}^{-1}\text{V}^{-1}$  for bridged  $\text{CN}_{\text{ads}}^-$ . This observation contrasts with what has been seen for linear and bridged  $\text{CO}_{\text{ads}}$  on palladium surfaces, wherein the Stark tuning rates for the two types of adsorbates are more similar.<sup>10</sup> The implication is that in the case of the Pd-CO system, it is an electrochemically induced Stark effect which gives rise to a potential dependent frequency change for the two types of adsorbed species. However, in the Pd-CN system, it is likely that changes in degree of back-donation from the metal to the adsorbate moiety (as the potential is changed) yield the observed potential-dependent frequency shifts that are observed.

An electrochemically induced Stark effect may also explain the above observations of differences in frequency potential

dependencies for cyanide in a linear vs. bridged site. It is possible that contribution from a surface "wall" effect leads to an increase in frequency that overcompensates the frequency decrease due to  $\pi$  back-donation.<sup>29</sup> Consider the case of  $\text{CN}^-$  adsorbed at a bridged site. The  $\text{C}\equiv\text{N}$  bond is weakened, which suggests back-donation into the  $\pi^*$  orbital of bridged  $\text{CN}_{\text{ads}}^-$ . Formation of a metal-carbon bond results in a smaller distance between the adsorbate and the surface plane. At an equilibrium distance from the surface the forces in balance are stronger for bridged  $\text{CN}_{\text{ads}}^-$  than for linear  $\text{CN}_{\text{ads}}^-$ , resulting in higher Pauli repulsion between closed shells (of surface metal and adsorbate species) against more strongly attractive electrostatic forces. The repulsive force varies exponentially with distance, so the wall effect is larger when the bridge-bound ion moves in an applied electric field; consequently the potential dependence of the frequency is larger. Conversely, for  $\text{CN}^-$  adsorbed at an on-top site the equilibrium bond length between the adsorbed ion and the metal surface is greater, so the repulsive force is less and the spatial gradient describing the attractive force is weaker. For  $\text{CO}_{\text{ads}}$ , electrostatic forces are less important since this species is not ionic, so the potential dependence of the frequency for linearly adsorbed species is greater than that of bridge-bound adsorbate.

We also observe that the relative and absolute intensities of the linear and bridged surface cyanide species show little or no concentration dependence. The only observable trend that was seen as the cyanide concentration was altered was a small increase in band frequency as the cyanide concentration decreased (Figures 4-6); this was observed for both linear and bridged species. Similar effects have been observed in Pd/CO systems in which coadsorbates served to decrease the band frequencies of adsorbed CO species.<sup>11</sup> The origin of such an effect is not well understood, and may be due to a combination of changes in dipole-dipole coupling between adsorbates, and to shifts in the potential of zero charge of the metal in systems of varying adsorbate concentration.

The behavior of bands due to the surface film near  $2150\text{ cm}^{-1}$  is similar in all three cases (Figures 4-6), while the  $2200\text{ cm}^{-1}$  band appears only in systems with relatively high cyanide concentration (Figure 6). The band near  $2150\text{ cm}^{-1}$ , ascribed previously to a surface  $\text{Pd}(\text{CN})_4^-$  species, appears at potentials near 0.0V (this onset potential is independent of cyanide concentration) and grows in intensity as the sample potential is made more positive. Concurrent with the appearance and growth of the surface feature near  $2150\text{ cm}^{-1}$  is the appearance of the solution feature at  $2135\text{ cm}^{-1}$ , which we have ascribed to dissolved  $\text{Pd}(\text{CN})_4^{2-}$ . This suggests that the surface feature at about  $2150\text{ cm}^{-1}$  is a precursor to the solution band at  $2135\text{ cm}^{-1}$ . It is interesting to point out that there is little electrochemical evidence for the formation and dissolution of the surface films seen in the PDIR spectra (Figure 1[a],[b]); the cyclic voltammograms are essentially flat within the voltage range studied, and a faradaic film formation may be so slow kinetically that it does not appear prominently in the voltammetry. It is possible therefore that an initial reaction of cyanide with the palladium surface takes place to form a surface Pd/CN complex prior to the imposition of an electrode potential. Then in the course of obtaining surface in situ IR spectra, the film becomes partially removed as the electrode potential is made more positive, and solution coordination compound is formed. However, we do not think that this compound formation occurs, since the electrode potential is cycled repeatedly before surface FTIR difference spectra are taken; such potential cycling ought to remove any surface film that would form spontaneously in the absence of an applied voltage.

The dependence of the intensity of various bands with electrode potential is contrary to the expectations based on chemical intuition. The bands at about  $2150$  and  $2200\text{ cm}^{-1}$  are a result of the formation of Pd/CN complexes, as previously mentioned. These complexes should be more abundant at the more positive electrode potentials. Yet the absorption bands observed from these species seem to indicate that these complexes are

present in higher concentration at more negative electrode potentials (see Figure 6, for example). This suggests that the PDIR spectra are not indicative of pure adsorption/desorption on the electrode surface. More likely we have some kinetic effect convoluted with the adsorption/desorption process.

We can postulate a type of kinetic effect which can lead to these spectra (e.g., Figures 5 and 6). When the spectra are collected, the potential is cycled between the sample and reference potentials. At the sample potential which is the more oxidative potential (i.e., more highly positive) we continue to form the Pd/CN complexes. These complexes appear to precipitate on the electrode surface in the form of a patchy, irregular film. A second process which occurs simultaneously is dissolution of the Pd/CN complex in solution. In the very early stages of the dissolution process only the solution in close proximity to the electrode surface has any significant amount of these complexes, leading to a bell-shaped concentration profile in the diffusion layer. As dissolution proceeds the region that shows this concentration gradient moves away from the surface. When we cycle to the reference potential that corresponds to the more negative potential the electrode now begins to reduce these complexes. The reduction begins at the electrode surface of the Pd/CN complex film and the analogous complexes dissolved in solution. The product of the reduction process is  $\text{CN}^-$  ions, so near the electrode surface the concentration of  $\text{CN}^-$  ions will be significantly higher than in bulk solution. We might expect the reduction process to proceed more slowly than the oxidation step. Furthermore, solvation of complexes and their diffusion away from the surface may continue during the initial stages of the reduction process. As a result, the depletion of the solvated complexes which will follow reduction of the film will proceed at the diffusion-controlled limit. It is quite likely that on the average the IR beam will see more Pd/CN complexes at the reference potential than at the sample potential. This observation could qualitatively explain why the bands corresponding to Pd/CN complexes show the observed intensity

variation. This work appears to be the first case where such a unique variation of PDIRS band intensities has been observed.

The classical model of Korzeniewski et al.<sup>12</sup> was used to calculate vibrational frequencies  $\nu_{C-N}$  and  $\nu_{Pd-C}$  for both linear and bridged cyanide species adsorbed on a palladium surface. The total energy of the system, which is the sum of the kinetic and potential energies, is expressed by the Hamiltonian:

$$H = \sum_i p_i^2 / 2m_i + \sum_j V_j , \quad [1]$$

The first summation includes only carbon and nitrogen atoms; although it is possible to include palladium vibrations as well, the effects of contributions from Pd-Pd vibrational interactions are negligible at this level of approximation. The potential energy consists of the sum of discrete interactions between atoms:

$$V_{tot} = V_{C-N} + V_{C-Surf} + V_{N-Surf} . \quad [2]$$

Here  $V_{C-N}$  and  $V_{N-Surf}$  are expressed by Morse potentials, and  $V_{C-Surf}$  is approximated by a Lennard-Jones potential, analogous to the case of CO adsorbed on a platinum surface.<sup>12</sup>

The parameters that were used in the  $CN'_{ads}$  potential interactions are summarized in Table I. The parameter  $r_0$  for the potential  $V_{N-Surf}$  (N-Pd interaction) was chosen to make this term repulsive,<sup>12</sup> and the remaining surface-atom interaction parameters (in  $V_{C-Surf}$  and  $V_{N-Surf}$ ) were chosen to yield the closest fit to experimentally determined vibrational frequencies (to within  $\pm 1 cm^{-1}$ ). Frequencies computed in this manner are compared with experimentally determined vibrational frequencies ( $\nu_{C-N}$ ) for linear and bridged  $CN'_{ads}$  on Pd in Table II. Experimental values of  $\nu_{Pd-C}$  are not listed since there are no experimental PDIRS data available for the palladium-cyanide system in the far infrared frequency range, and SERS data in this spectral region are only available for cyanide on gold<sup>36</sup> and silver<sup>37</sup> surfaces. Binding



energies for linear and bridged  $\text{CN}_{\text{ads}}^-$  were calculated as the difference between total energy (from Eq. 2) and the dissociation energy of an isolated cyanide ion.<sup>38</sup> These values were estimated to be 1.4 and 2.0 eV for linear and bridged species, respectively. The computed binding energies for  $\text{CN}_{\text{ads}}^-$  species are smaller than those estimated for adsorbed CO on Pt,<sup>12</sup> and reflect the greater degree of ionic bonding in the case of cyanide on palladium vs. predominately covalent bonding for the case of carbon monoxide on platinum.<sup>26</sup>

The potential dependency of the C-N stretching frequency on applied potential for linear and bridge-bound  $\text{CN}_{\text{ads}}^-$  on Pd was estimated by applying a perturbation which represents the effects of an applied electric field.<sup>12,39,40</sup> This field is added to the interaction potential, and has the form:

$$V_{\text{field}} = E_z d\mu/dz (z^0 - z) , \quad [3]$$

where  $E_z$  is the electric field strength perpendicular to the electrode surface,  $d\mu/dz$  is the dipole moment derivative normal to the surface, and  $(z^0 - z)$  represents the relative normal displacement of an atom from its equilibrium position. The experimental value of  $d\mu/dz$  (2.4 D/Å) is available in the literature,<sup>41</sup> and differs appreciably from theoretically predicted values, which are higher.<sup>42</sup> From these quantities the potential dependencies of the band frequencies ( $dv_{\text{C-N}}/dE$ ) were estimated to be  $8\text{ cm}^{-1}\text{V}^{-1}$  and  $15\text{ cm}^{-1}\text{V}^{-1}$  for linear and bridged  $\text{CN}_{\text{ads}}^-$ , respectively. While these estimated values are somewhat less than those observed experimentally, they give qualitative agreement with the fact that  $dv_{\text{C-N}}/dE$  is greater for the bridged adsorbate than for the linearly adsorbed species. It is also of interest to note that the frequency shift with potential of the C-N stretch from linear  $\text{CN}_{\text{ads}}^-$  on Pd is less than that for linear  $\text{CO}_{\text{ads}}$  on Pt.<sup>43</sup> Since the value of  $d\mu/dz$  is appreciably smaller for cyanide than for carbon monoxide (this quantity is approximately 3.1 D/Å for gas phase CO),<sup>44</sup> a smaller frequency potential dependence is to be expected for the adsorbed cyanide species.

## CONCLUSION

Surface-sensitive in situ FTIR difference spectra of cyanide adsorbed on polycrystalline palladium in perchlorate electrolyte give strong evidence for the predominance of bonding to a two-fold bridged site on the electrode surface throughout most of the double-layer region. At far negative potentials the relative abundances of linear and bridged  $\text{CN}_{\text{ads}}^{\cdot}$  species are comparable, but as the potential is made more positive the intensity of the IR band due to bridged  $\text{CN}_{\text{ads}}^{\cdot}$  becomes much greater than that due to linear  $\text{CN}_{\text{ads}}^{\cdot}$ . Surface Pd/CN bands that are precursors to solution palladium cyanide complexes were detected by the PDIR technique, while no evidence for the existence of these species was obtainable by conventional electrochemical methods. The band frequency  $\nu_{\text{C-N}}$  due to linear  $\text{CN}_{\text{ads}}^{\cdot}$  on Pd is lower than that observed previously on other electrode surfaces (e.g., Pt, Ag, Au, Cu), suggesting a higher degree of covalent bonding on Pd compared to the other metals.

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TABLE I. Morse and Lennard-Jones parameters used in the interaction potential for linear and bridged  $\text{CN}_{\text{ads}}$  on a Pd surface.

Morse Parameters:

	$D_e$ (eV)	$\alpha$ ( $\text{\AA}^{-1}$ )	$r_0$ ( $\text{\AA}$ )
Linear $\text{CN}_{\text{ads}}$			
C-N	2.31 <sup>30</sup>	2.354 <sup>30,31</sup>	1.166 <sup>32</sup>
N-Pd	0.131 <sup>33</sup>	0.850 <sup>33</sup>	4.60 <sup>12</sup>
Bridged $\text{CN}_{\text{ads}}$			
C-N	7.991 <sup>32</sup>	2.13 <sup>31</sup>	1.166 <sup>32</sup>
N-Pd	0.102 <sup>33</sup>	0.65 <sup>33</sup>	4.60 <sup>12</sup>

Lennard-Jones Parameters:

	$\epsilon$ (eV)	$\sigma$ ( $\text{\AA}$ )
Linear $\text{CN}_{\text{ads}}$		
C-Pd	2.25 <sup>34</sup>	1.81 <sup>35</sup>
Bridged $\text{CN}_{\text{ads}}$		
C-Pd	2.05 <sup>33</sup>	1.70 <sup>12</sup>

TABLE II. Vibrational frequencies  $\nu_{C-N}$  and  $\nu_{Pd-C}$  for linear and bridge-bound  $CN_{ads}$  on Pd.

	Calc'd freq (cm <sup>-1</sup> )	Expt'l freq (cm <sup>-1</sup> )
Linear $CN_{ads}$ :		
$\nu_{C-N}$	2055	2060
$\nu_{Pd-C}$	416	---
Bridged $CN_{ads}$ :		
$\nu_{C-N}$	1981	1972
$\nu_{Pd-C}$	234	---

## FIGURE LEGENDS

Figure 1. Cyclic voltammograms for (a) 1mM NaCN in 0.10M NaClO<sub>4</sub>, (b) 25mM NaCN in 0.10M NaClO<sub>4</sub>, and (c) 0.10M NaClO<sub>4</sub> obtained at a palladium electrode. Sweep rate = 50mVs<sup>-1</sup>.

Figure 2. In situ PDIR spectra (2000 scans) of NaCN (25mM) in 0.10M NaClO<sub>4</sub> on polished palladium surface. Solid line: combined SNIFTIRS/IRRAS spectrum (see text for experimental details); dashed line: SNIFTIRS spectrum, s-polarized radiation. The reference potential was -0.90V vs. Ag/AgCl, and the sample potential was +0.70V vs. this reference. See text for details concerning the collection of the FTIR difference spectra.

Figure 3. Schematic showing possible structures for linear and bridged CN<sub>ads</sub><sup>-</sup> on a Pd electrode.

Figure 4. Surface-sensitive in situ PDIR spectra (combined SNIFTIRS/IRRAS, 2000 scans) of 1mM NaCN in 0.10M NaClO<sub>4</sub> obtained at a palladium electrode as a function of applied potential (vs. Ag/AgCl). The reference potential was -0.90V vs. Ag/AgCl.

Figure 5. Same as Figure 4, except [NaCN] = 5mM.

Figure 6. Same as Figure 4, except [NaCN] = 25mM.

Figure 7. Plot of peak position (in cm<sup>-1</sup>) vs. applied potential (V) for  $\nu_{C-N}$  of linearly- and bridge-bound CN<sub>ads</sub><sup>-</sup> on Pd for 1, 5, and 25mM NaCN in 0.10M NaClO<sub>4</sub>. Open circles: 1mM NaCN; closed circles: 5mM NaCN; triangles: 25mM NaCN. Potentials vs. Ag/AgCl.



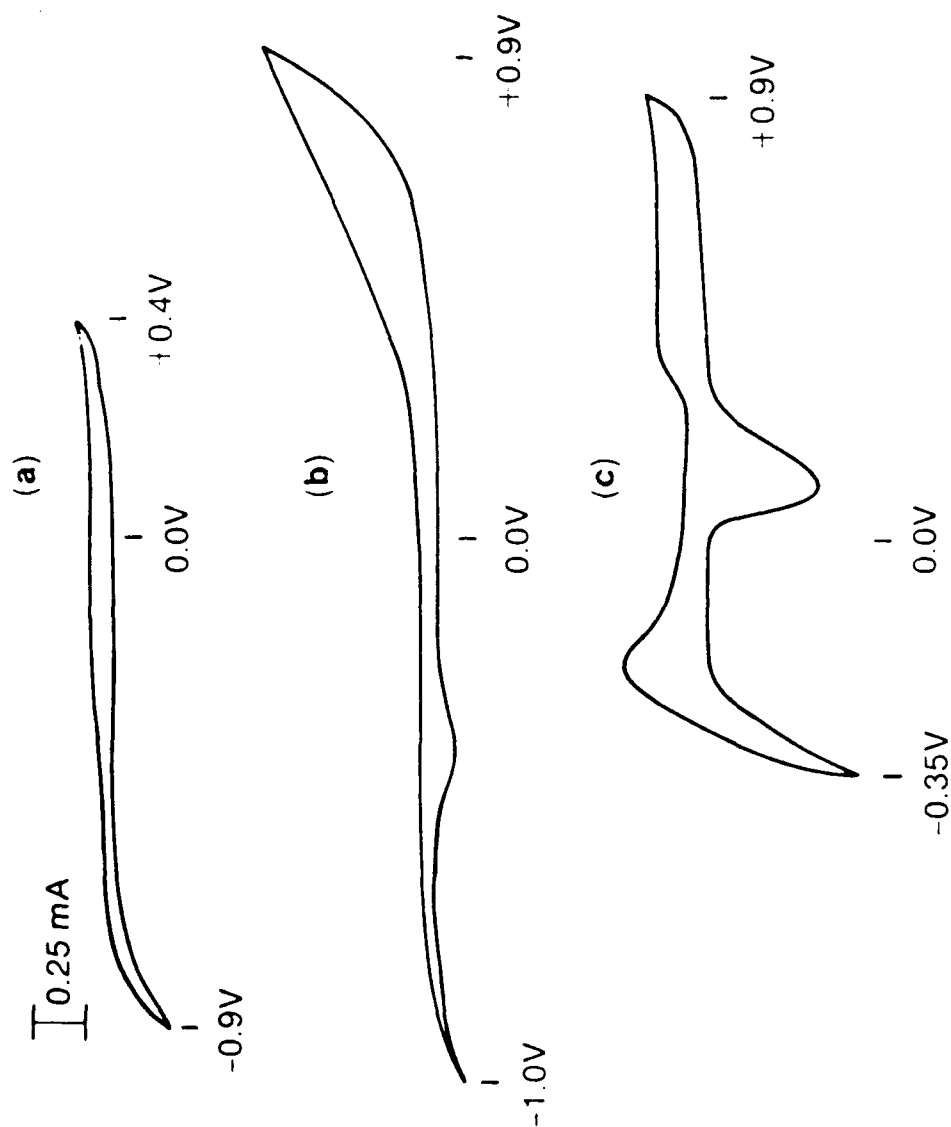


Fig. 1

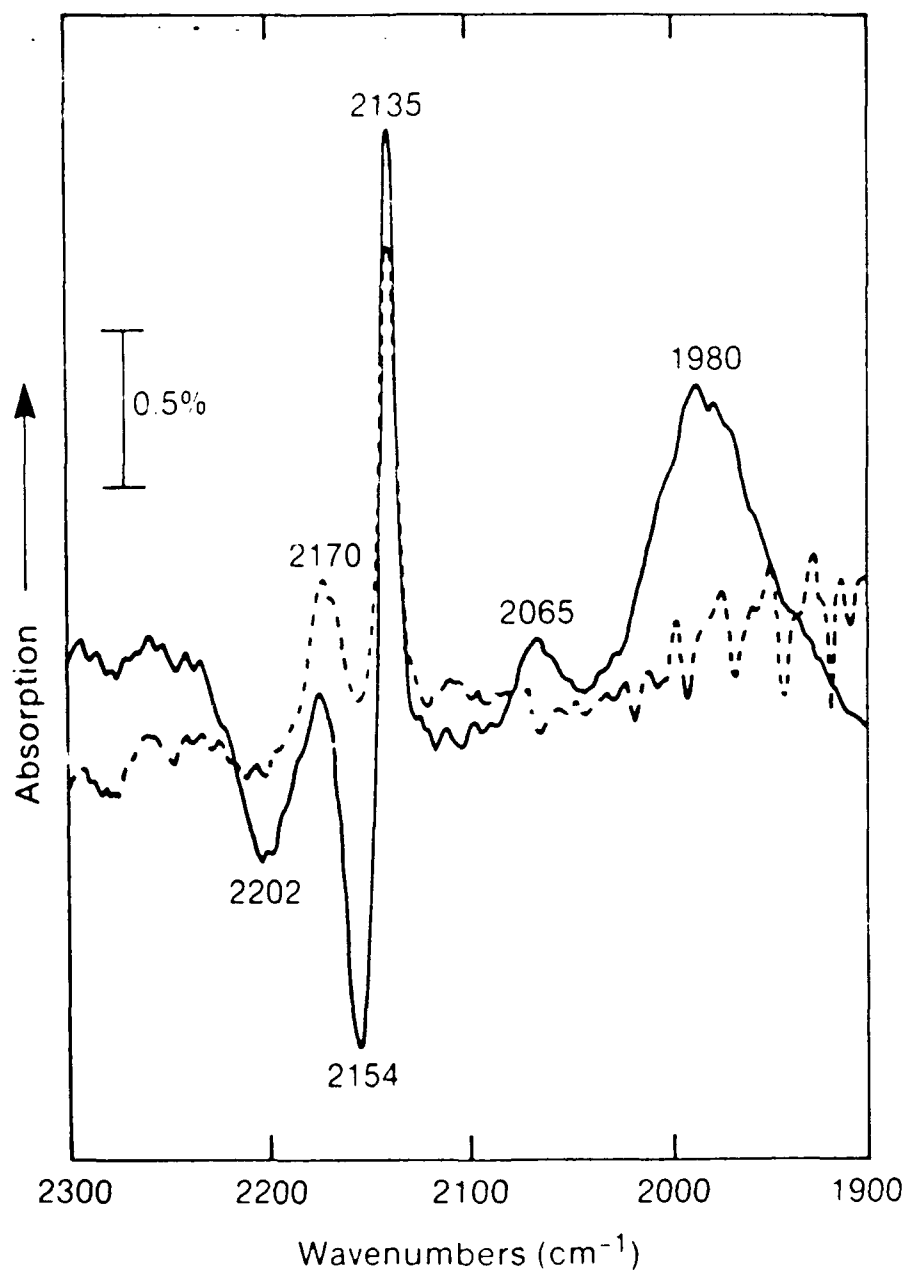


Fig. 2

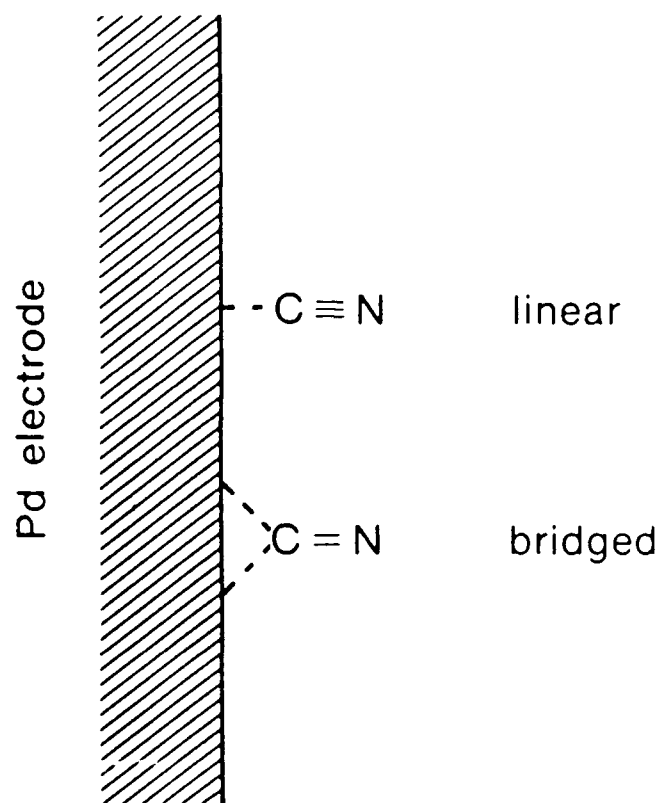


Fig. 3

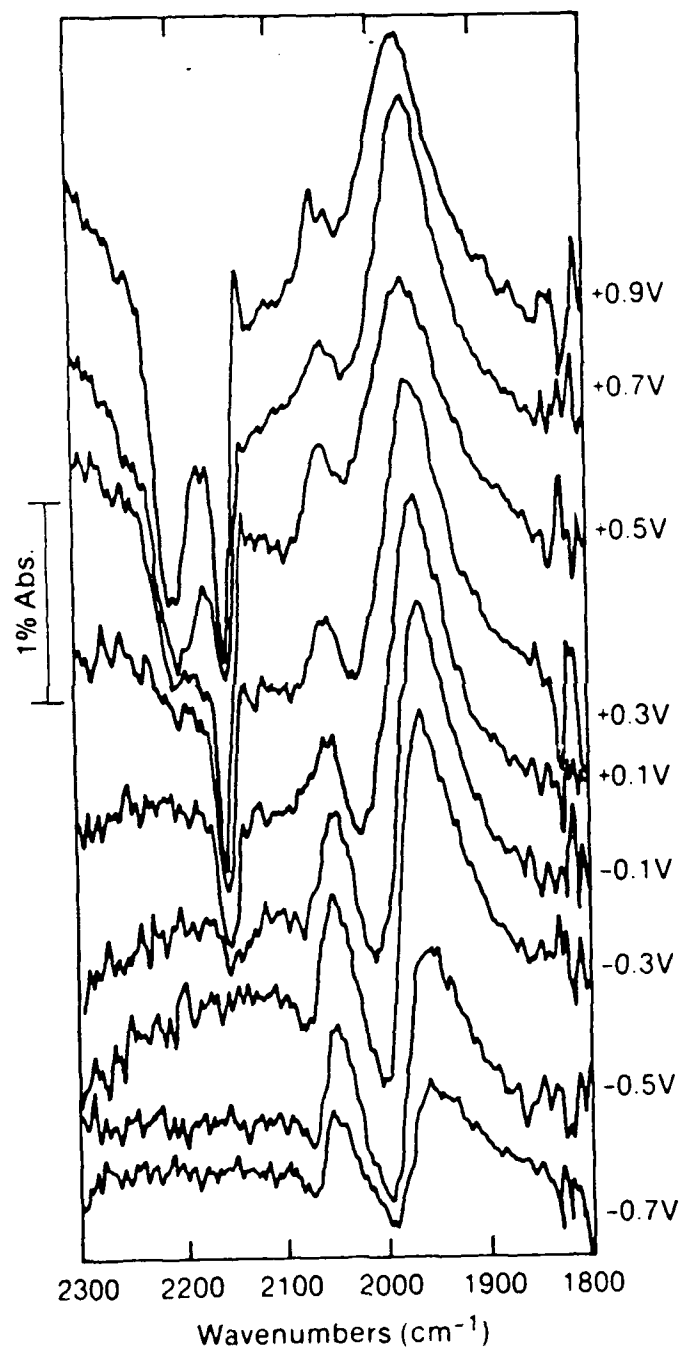


Fig. 4

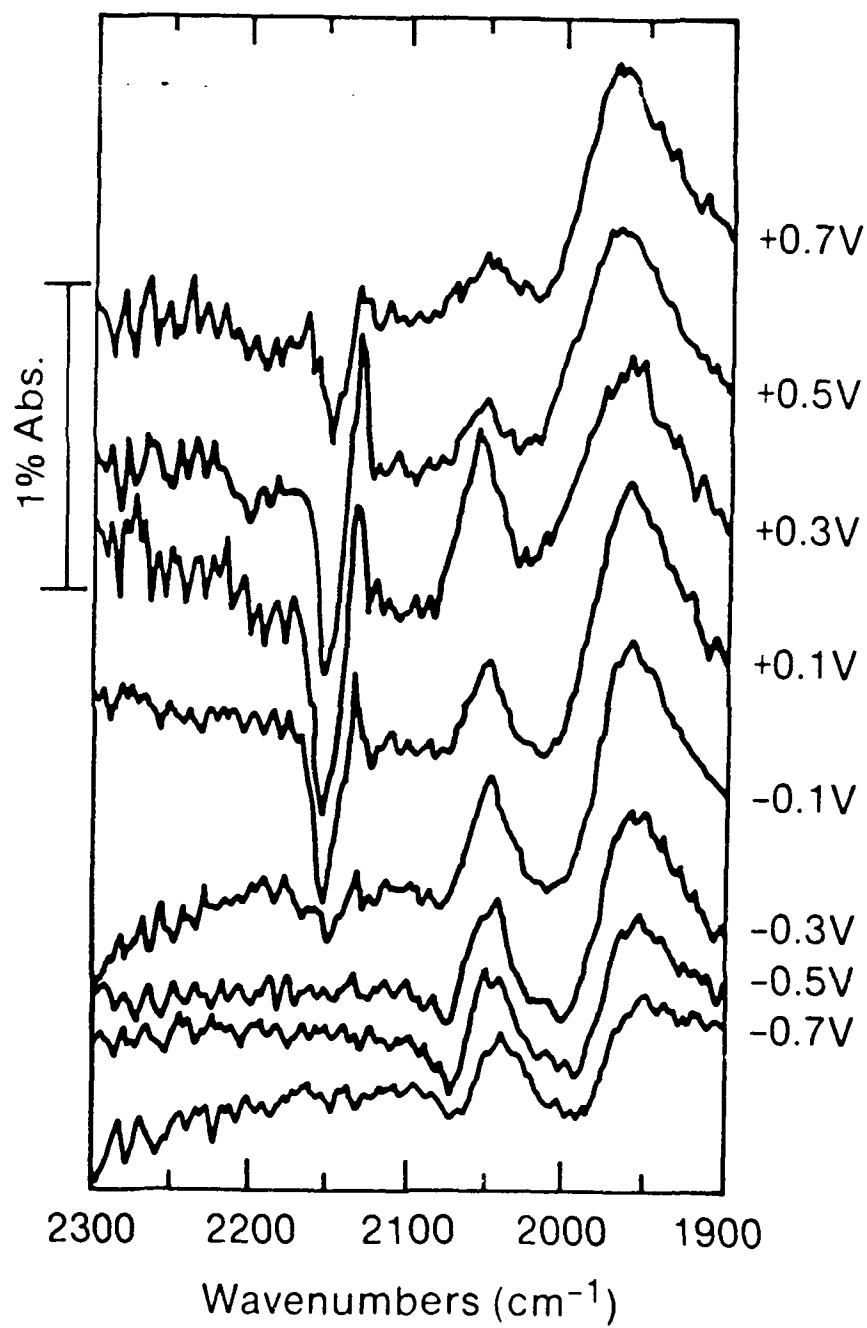


Fig. 5

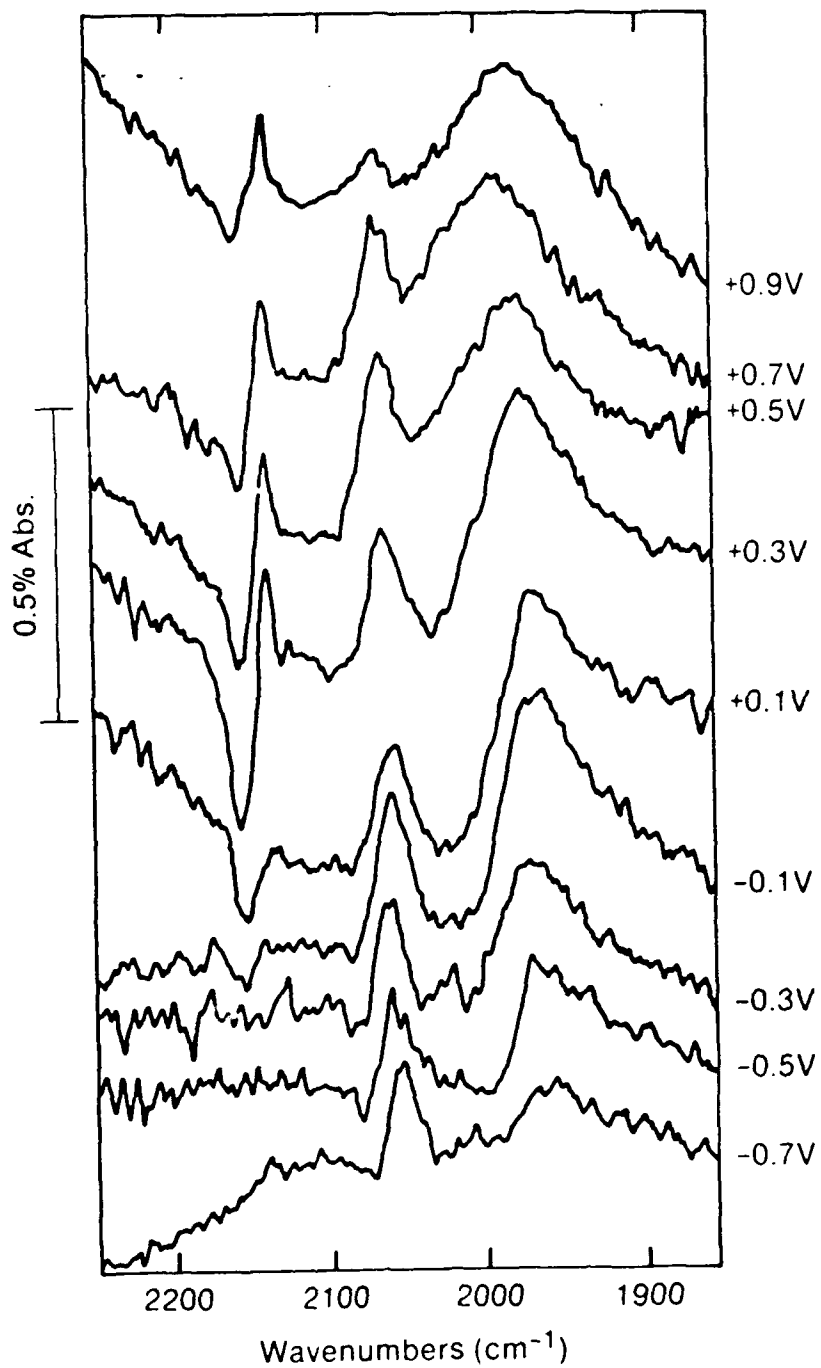


Fig. 6

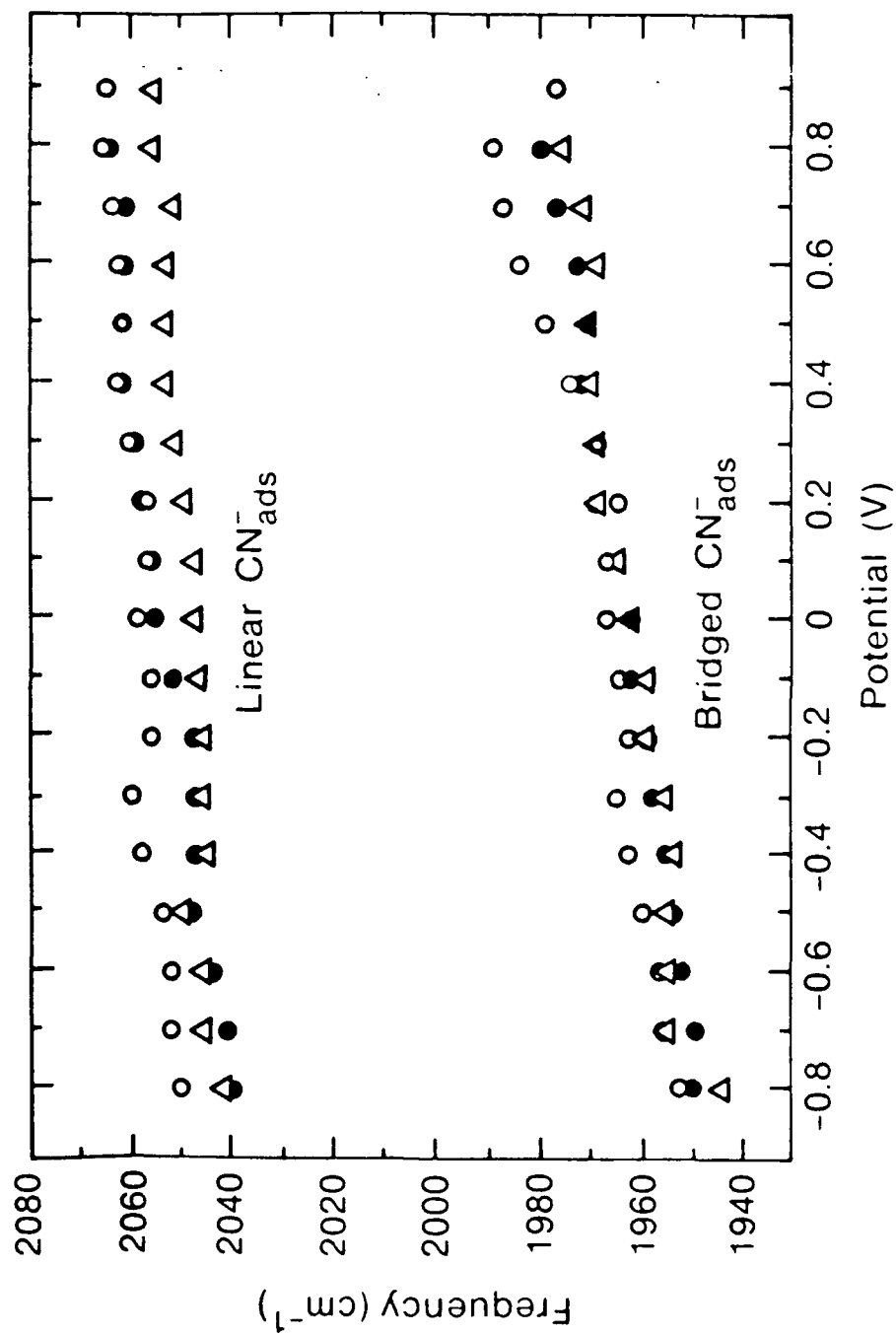


Fig. 7